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Graphite Immobilisation in Glass Composite Materials

Mohd Zul Hilmi Mayzan

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Immobilisation Science Laboratory
Department of Materials Science and Engineering
The University of Sheffield

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Abstract

Irradiated graphite is a problematic nuclear waste stream and currently raises significant concern worldwide in identifying its long-term disposal route. This thesis describes the use of glass materials for the immobilisation of irradiated graphite prepared by microwave, conventional and sparks plasma sintering methods. Several potential glass compositions namely iron phosphate, aluminoborosilicate, calcium aluminosilicate, alkali borosilicate and obsidian were considered for the immobilisation of various loadings of graphite simulating irradiated graphite. The properties of the samples produced using different processing methods are compared selectively. An investigation of microwave processing using an iron phosphate glass composition revealed that full reaction of the raw materials and formation of a glass melt occurs with consequent removal of porosity at 8 minutes microwave processing. When graphite is present, iron phosphate crystalline phases are formed with much higher levels of residual porosity of up to 43 % than in the samples prepared using conventional sintering under argon. It is found that graphite reacts with the microwave field when in powder form but this reaction is minimised when the graphite is incorporated into a pellet, and that the graphite also impedes sintering of the glass. Mössbauer spectroscopy indicates that reduction of iron occurs with concomitant graphite oxidation. The production of graphite-glass samples using various powdered glass compositions by conventional sintering method still resulted in high porosity with an average of 6-17 % for graphite loadings of 20-25 wt%. Due to the use of pre-made glasses and controlled sintering parameters, the loss of graphite from the total mass is reduced compared to the microwaved samples; the average mass loss is < 0.8 %. The complication of iron oxidation and reduction is present in all the iron containing base glasses considered and this increases the total porosity of the graphite-glass samples. It is concluded that the presence of iron in the raw materials or base glasses as an encapsulation media for the immobilisation of the irradiated graphite waste is not advisable. The production of glass and graphite-glass samples based calcium aluminosilicate composition by spark plasma sintering method is found highly suitable for the immobilisation of irradiated graphite wastes. The advantages of the method includes short processing time *i.e.* < 40 minutes, improved sintering transport mechanisms, limited graphite oxidation, low porosity (1-4 %) and acceptable tensile strength (2-7 MPa). The most promising samples prepared using spark plasma sintering method were loaded with 30-50 wt% graphite.

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Conferences

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Contents

1. Introduction

The maintaining, decommissioning and dismantling of certain types of nuclear power plants used to generate electricity are mainly responsible for the production of problematic irradiated graphite wastes. Currently, the conditioning and disposal plan for the irradiated graphite waste remains unclear in all waste producing countries (*i.e.* UK, Russia, US, France). The major concern related to the irradiated graphite is the huge volume of the waste, which accounted worldwide about 260 000 tonnes and the present of long-lived radionuclides *i.e.* ^{3}H, ^{14}C, ^{16}Cl. Historically relative little attention has been given to identifying a disposal strategy for irradiated graphite waste. The irradiated graphite waste now urgently requires disposal management solutions and this triggered interest in studying immobilisation methods that may be suitable for the production of irradiated graphite wasteform based glass materials.

A survey of the literature reveals several potential immobilisation methods that may suitable for the production of graphite glass composite wasteforms. This leads to the novel aim of the thesis; to investigate the potential of glass materials as a host for the production of irradiated graphite wasteforms prepared using unconventional and conventional processing methods. The aim can be divided into three primary research objectives as follow:

i. To assess the potential of microwave processing method for the production of graphite wasteforms using iron phosphate glass.
ii. To explore and assess the potential of conventional sintering in the production of graphite wasteforms prepared using various glass systems as a host.
iii. To investigate the potential of spark plasma sintering method for the production of graphite wasteforms using calcium aluminosilicate glass.

In order to achieve the mentioned aim and objectives, the thesis is structured and organised into six further chapters including literature review and theory, materials and experimental methods, result and discussion I, result and discussion II, result and discussion III and finally conclusion and suggestions for further work. Chapter 2 provides the background of nuclear power reactors as a source of radioactive wastes and particular focus is given to irradiated graphite waste; the

structure, properties, waste origin and problems arising from the irradiated graphite waste are reviewed. Attention is also given to recognise the suitability and materials processing techniques of microwave, conventional sintering and spark plasma sintering for the production of graphite-glass wasteforms.

Chapter 3 presents a description of graphite simulant and details about immobilisation methods used and processing methods employed throughout the preparation of graphite-glass composite wasteforms. All the basic principles of the instruments and the materials characterisation techniques conducted on the produced samples are explained in detail. This includes a variety of analytical techniques used such as particle size analysis, thermogravimetric analysis, differential thermal analysis, dilatometry, chemical analysis, volume shrinkage, assessing mass loss, density, porosity, X-ray diffraction, fourier transform infrared spectroscopy, microscopy, Raman spectroscopy, Mössbauer spectroscopy and indirect tensile testing – Brazilian method.

Results and discussion are split into three chapters and structured accordingly to each of the research objectives. Chapter 4 gives the characterisation results of graphite simulant, iron phosphate glass and composite wasteforms prepared using microwave as well as a comparison of potential microwave samples with samples produced using conventional sintering. Findings from Chapter 4 lead to the development of Chapter 5, which discussed the use of various glass compositions as a host to encapsulate graphite simulant. The iron phosphate glass composition is used as a baseline in comparing with the results obtained using other glass compositions namely alumino-borosilicate, calcium aluminosilicate, modified alkali borosilicate and obsidian. Based on Chapter 4 and 5, Chapter 6 was developed and specifically focuses on the production of low porosity graphite-glass wasteforms using calcium aluminosilicate glass. The obtained data were compared with the sample produced using conventional sintering.

The key findings from the results and discussion chapters are summarised in Chapter 7. In this chapter, future works and recommendations are also presented as guidelines to identifying an ideal wasteform for the immobilisation of irradiated graphite waste.

2. Literature Review and Theory

2.1. History, Current and Future Usage of Nuclear Technology

In 1932, James Chadwick discovered the neutron (Chadwick 1932). The next year Enrico Fermi found a much greater variety of artificial radionuclides was formed when using neutrons instead of protons as a source for bombarding the atoms. The history of nuclear fission started at the end of 1938, when Otto Hahn and Fritz Strassmann attempted to create transuranic elements by bombarding uranium with neutrons. They expecting heavy elements, however, the product produced from the experiment were lighter elements including ^{141}Ba and others which were about half the mass of uranium. This result was interpreted by Lise Meitner and Otto Frisch working under Neil Bohr (Meitner and Frisch 1939); they suggested that the neutron was captured by nucleus and causing severe vibration leading to the nucleus splitting into two roughly equal parts which termed fission (essentially the fission of ^{235}U had occurred). In 1939, Otto Frisch successfully confirmed that the fission of ^{235}U yielded numerous amount of energy, ~200 MeV (Frisch 1939) and realised the potential of a fission chain reaction. This was the first experiment confirming the theory of Albert Einstein, which explained the equivalence between mass and energy, $E = mc^2$ (Einstein 1905).

Motivated from the neutron-induced fission, and thus potentiality of fission chain reaction to generate huge amounts of energy in a short time period, Enrico Fermi and co-worker developed the first man-made nuclear reactor (Chicago pile 1, originally known as 'atomic piles') with self sustaining nuclear fission chain reaction on 2 Dec 1942. The reactor utilised natural abundance of U, was graphite moderated, and controlled by a removable Cd neutron absorber; in order to achieve criticality (balance of neutrons for sustaining nuclear fission chain reaction), the crude reactor used 6 tonnes of uranium metal, 50 tonnes of uranium oxide and ~400 tonnes of graphite (Greenwood and Earnshaw 1997). It is unfortunate that the first nuclear reactor was purposely aimed to build nuclear weapons as part of Manhattan Project, evidenced in Trinity test explosion (16th July 1945) and controversial dropping of two atomic bombs to end World War II with Japan (6,9th August 1945). Nevertheless, it is evidence that graphite has been used in nuclear technology from the earliest days.

The new era of nuclear reactors used for generating electricity began in the 1950s and they have been improved ever since. The first nuclear reactor to generate electricity was built in a small scale by Argonne National laboratory, Idaho, USA in 1951. The reactor was called Experimental Breeder Reactor (EBR-1) and successfully powered four 100 W light bulbs. At present, more than 400 nuclear reactors are being used to generate electricity and the reference data of operated reactors connected to the grid at the end of 2013 is listed in Table 2-1. Note that the graphite is continuously used as moderator in current operated gas-cooled and light water graphite reactors.

Table 2-1: Nuclear power reactors in commercial operation, 31 Dec 2013 (IAEA 2014b).

Reactor type	Main countries	Number	GWe	Fuel	Coolant	Moderator
Pressurised Water Reactor (PWR)	US, Fance, Japan, Russia, China	273	253	Enriched UO_2	Water	Water
Boiling Water Reactor (BWR)	US, Japan, Sweeden	81	76	Enriched UO_2	Water	Water
Pressurised Heavy Water Reactor 'CANDU' (PHWR)	Canada	48	24	Natural UO_2	Heavy Water	Heavy Water
Gas-cooled Reactor (AGR, Magnox)	UK	15	8	Natural U metal, enriched UO_2	CO_2	Graphite
Light Water Graphite Reactor (RBMK, EGP)	Russia	15	10.2	Enriched UO_2	Water	Graphite
Fast Neutron Reactor (FBR)	Russia	2	0.6	PuO_2 and UO_2	Liquid Sodium	None
Total		434	~372			

The electricity supply from nuclear reactors worldwide is estimated to be about 11.3 % in 2013; the other types of energy sources generating electricity are estimated to contribute about 68.5,

17.8, and 2.4 % for thermal (solids, liquids, gasses, biomass and waste), hydro and renewable (geothermal, wind, solar, tide) energy respectively (IAEA 2014a). The use of nuclear power reactors to generate electricity is gaining attention as it makes significant contribution to the mitigation of green-house gas emissions *e.g.* in 2009, it was claimed that the nuclear power reactors reduced by about 10 % of CO_2 emission from the world energy consumption (Adamantiades and Kessides 2009, Menyah and Wolde-Rufael 2010). Furthermore the use of a small amount of fuel, improved design of reactor and reliable energy source making the nuclear reactors favourable technology among the others in terms of generating electricity.

It is clear that the global plan is to reduce the CO_2 emissions, minimise the green-house gases and consequently decrease the amount of manmade global warming. This means that the use of coal thermal power plan will be further reduced and to meet the demand for electricity consumption that keeps increasing (global energy demand is estimated to increase by ~37 % by 2040), the use of nuclear, hydro and renewable energy is being increased (IEA 2014b). It is also evidence in the past (from 1973-2012) that the total global electricity demand is increased from 9.4 to 18.1 % (IEA 2014a). As a result, more nuclear reactors are being built and are planned to be built in the future. In 2013 alone, 77 nuclear reactors were under construction and 48 of those reactors were located in Asia (IAEA 2013). This is the highest number of reactors being constructed since 1989 and the figure is more likely to increase in the future, which may account for ~17 % of the global electricity production in 2050 (OECD *et al* 2015). Furthermore generation IV nuclear reactors (expected to arrive in ~2030) such as prismatic and pebble bed designed High Temperature Gas-cooled Reactor (HTGR) also utilise graphite as a reactor core and fuel matrix – tristructural-isotropic (TRISO) fuel and fuel pebble (OECD Nuclear Energy Agency 2014). Thus one can predict that more irradiated graphite will be produced in the future.

2.2. Commercial Nuclear Power Reactor

Commercial nuclear power reactors generate electricity by converting thermal energy from nuclear fission reactions (heat generated from kinetic energy of fission products, absorption of gamma rays and radioactive decay from fission products) to mechanical energy. In principle, the process usually initiated by transferring heat to coolant and then water to produce high pressure

steam of which used to rotate the multiple blades in the turbine. The turbine is designed to minimise the energy lost and capable to condense the steam back into water so that the cycle could operate continuously. The kinetic energy created from the rotation of blades in the turbine is converted into electrical energy by a generator. Essentially, all the nuclear power reactors utilise similar concepts to generate electricity and schematics of the most popular commercial reactors to date is shown in Figure 2-1. Note that the turbine and generator parts of the reactors are not shown in the figure.

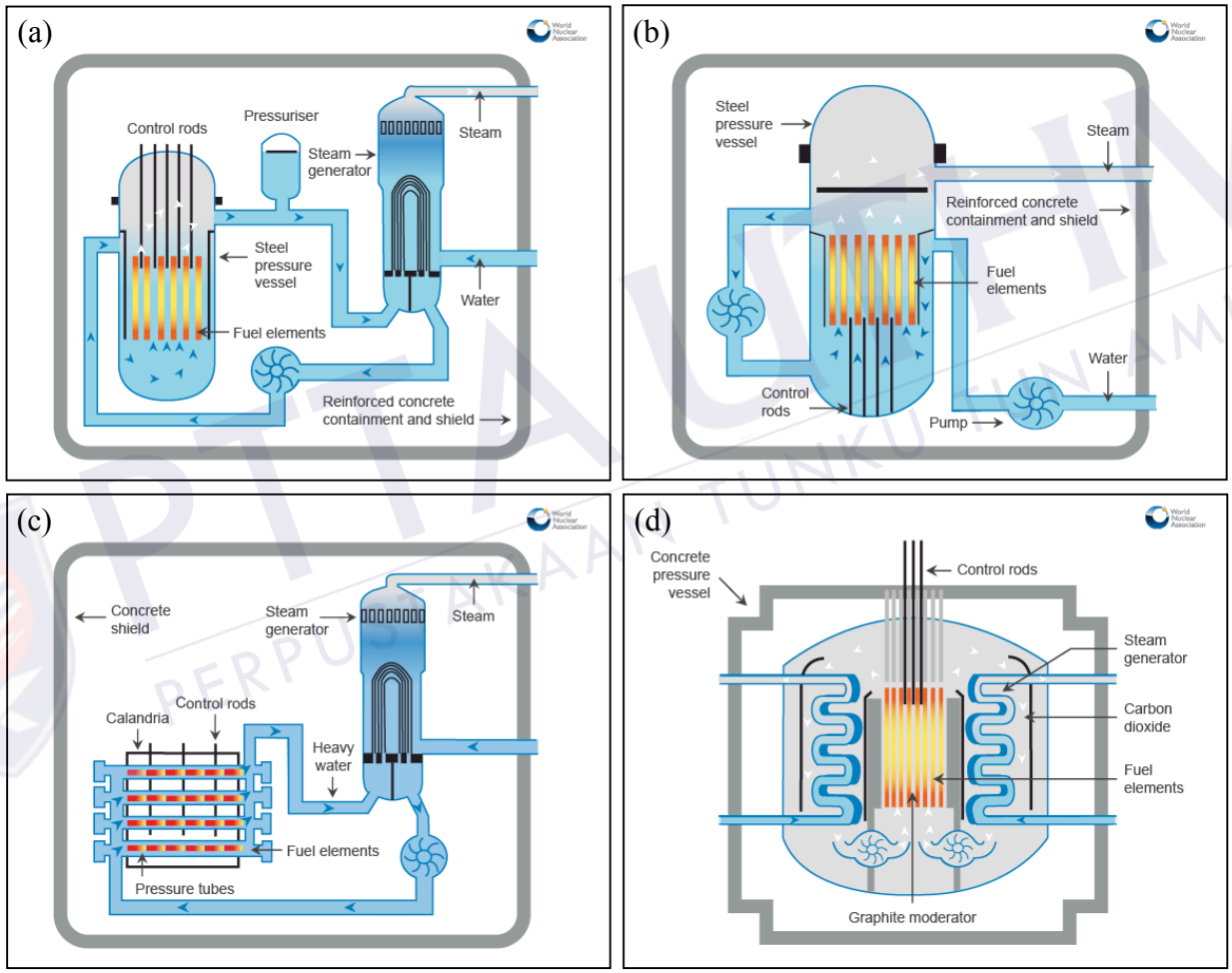

Figure 2-1: Schematic of currently used nuclear reactors, (a) PWR, (b) BWR, (c) PHWR/Candu and (d) AGR (taken from WNA 2015).

2.2.1. Main Components

The nuclear power reactors currently used for generating electricity can be categorised into 2 types: fast and thermal (slow) reactors. Unlike the explosion of nuclear weapons, nuclear power reactors are meant to control the nuclear fission activity and sustain the nuclear chain reaction as well as maintaining the production of electricity in a long term condition; the expectation of lifespan is ~30-40 years. As evidenced in Table 2-1, the use of fast reactors (FBR) is less favourable compared to the thermal reactors (PWR, BWR, PHWR, AGR, Magnox, RBMK, EGP). The reason behind this is solely because fast reactors are difficult to build and very expensive to operate, although fast reactors are capable of generating ~60 times energy than thermal reactors. In spite of both reactors are technically different, most of the reactors components are largely similar and can be simplified as follows (Duderstadt and Hamilton 1976, Wilson 1996, IAEA 2007, Stacey 2007, Lewis 2008):

Fuel (fissile element) – The main difference between both fast and thermal reactors are the types of fuels. A fast reactor usually employs enriched ^{239}Pu or enriched ^{235}U (require about 20-30% of fissile nuclei) core surrounded with ^{238}U (fissionable/fertile element) blanket. This type of reactor generates more fuel than it consumes; this occurs because ^{238}U has high probability to capture a fast neutron from the fission of ^{239}Pu or ^{235}U, neutrons induced by fission are then captured by ^{238}U and consequently breed ^{239}Pu as well as releasing two β-decays (Cochran *et al* 2010). The new generated ^{239}Pu radionuclides can later be utilised as new fuel in future reactors. In contrast, thermal reactor mainly uses natural uranium (contained ~0.7 ^{235}U) or enriched ^{235}U (up to 5 % of ^{235}U) fuel. Generally the fuel is fabricated into pellets, being vertically arranged/stacked in a cladding tube (*i.e.* zircaloy, stainless steel, Mg alloy) called fuel rod and numerous fuels rod form the fuel assembly that specifically designed to be lifted into and out of the reactor core. To start the nuclear fission reaction, a neutron is captured by a fissile nucleus and the reactions occurring from ^{235}U or ^{239}Pu are given in Equation 2-1 and 2-2 respectively. Note that Equation 2-1 and 2-2 are the fissions caused by the thermal neutron without considering the energy from neutrinos.

$$^{235}\mathrm{U} + \text{neutron} \rightarrow \text{fission fragments} + 2.4\,\text{neutrons (average)} + 192.9\ \text{MeV} \qquad [2\text{-}1]$$

$$^{239}\text{Pu} + \text{neutron} \rightarrow \text{fission fragments} + 2.9\,\text{neutrons (average)} + 198.5\ \text{MeV} \quad [2\text{-}2]$$

Moderator – In a fast nuclear reactor, the use of moderator is not necessary because the reactor utilises fast neutrons to cause fission in their fuel. Due to the low probability of fission versus neutron capture, the highly enriched fissile fuel is used to sustain the chain reaction. However, in the thermal reactors, the fast neutrons (resulting from fission) must be slowed by the moderator; as fast neutrons (kinetic energy ≥ 1 MeV) are most likely to be captured by ^{238}U, which is non-fissile. Only the thermal neutrons (kinetic energy < 1 eV) have a high cross-section (probability) to efficiently maintain and sustain the fission reaction of ^{235}U. Theoretically, the neutrons are slowed by collisions with nuclei of about similar mass and these materials are not neutron absorbers. The common moderators used to date are ordinary water and purified graphite as well as the most excellent one but expensive heavy water. For gas-cooled nuclear power reactors *i.e.* AGR and Magnox, purified graphite is the most suitable material and widely used as a moderator. In fact the voluminous irradiated graphite waste largely originates from moderator part of nuclear power plant.

Control Rod – The purpose of control rod is to maintain the rate of fission chain reaction, so that the nuclear power reactor achieves criticality and operates at a steady power level. To control the rate of fission reaction, neutron-absorbing materials whose nuclei absorb neutrons without undergoing any addition reaction, such as B, Cd or Hf are used for the production of control rods. The control rods are being inserted or withdrawn from the reactor core to control the number of the neutrons; absorbing more neutrons means that less neutrons are available for nuclear fission, thus inserting the control rod deeper into the reactor core will reduce the power output of the nuclear reactor and vice versa. The control rod is also used to halt the nuclear power reactor by absorbing all the neutrons to stop the fission reactions.

Coolant – Nuclear reactor coolant circulating around the reactor core and is primarily used to remove and transfer the heat energy from the core to generate steam. The coolant must be mobile in nature, hence only satisfied by liquid or gas materials. In fast reactors, the use of moderator type coolants (water, heavy water) is not possible as water can moderate the fast neutron. In addition, the more compact core of fast reactor produces high temperature that cause severe

cooling problems, thus a more efficient coolant such as liquid Na or Pb is used. In thermal reactors, ordinary water, heavy water (water usually pressurised to maintain at liquid phase) or CO_2 gas are commonly used as a coolant. All the thermal reactors except BWR type separate the cooling system from the water that will be boiled to produce high pressure steam.

Pressure Vessel or Protective vessel – Fast reactors do not utilised pressurised coolant, thus the protective vessel is used as containment for its coolant and reactor core. In the thermal reactors, a steel pressure vessel (PWR, BWR, AGR, Magnox) or pressure tubes (PHWR) is used to hold the circulated pressurised coolant as well as acting as containment for the moderator, control rods (except PHWR) and reactor core (see Figure 2-1). The pressure vessel/tube or protective vessel also worked as the first layer of shielding; preventing most of the radiation and radionuclides from leaching out to the biological environment. In some cases, a reflector is installed inside the vessel or surrounding the core to reflect the scattered neutrons back to the reactor core (Duderstadt and Hamilton 1976); this increases the efficiency of the fission of the fuel and at the same time protects the vessel from neutron induced damage which decreases the lifespan of the vessel. Characteristically, the reflector possesses similar properties to the moderator and sometimes similar materials serve a dual purpose in the nuclear power reactor. The most common material used as a reflector is graphite.

Steam Generator – This component is specifically designed as a heat exchanger, which converts water into steam. The steam generator is constructed separately in fast and thermal reactors. Only BWR (thermal reactor) boils the water in a pressurised vessel and directly uses steam generated in-situ by this process.

Containment and Shielding – The purpose of containment and shielding is to protect the atmosphere and biological environment from contamination by radionuclides and radiation as well as acting as a safety system if any malfunctions of the components occur inside the reactors. Nuclear reactors are a source of intense radiation and contain radioactively contaminated components/systems, the whole reactor apart from the turbine (excluding BWRs) must be isolated and shielded from the biological system. A BWR usually needs a complete containment and shielding due to the whole components including the turbine containing radioactive

materials. Typically, a metre thick reinforced concrete or steel/lead structure is used as containment and shielding in current commercial reactors.

Turbine and Generator – The turbine and generator are the key components to generate electricity from the nuclear energy and these components are being installed in all types of commercial nuclear reactors. In practice, the high pressure steam turns the turbine and the generator converts the produced mechanical energy to electrical energy by using an electromagnetic field. The produced electrical energy is then manipulated by the transformers, connected to the grid and supplied to the consumers.

2.3. Nuclear Wastes

Nuclear power reactors are a mature technology and have been proven safe while generating reasonably clean electrical energy. The drawback of using nuclear power reactor is the fact that the nuclear reactor creates significant amount of radioactive waste from the fission process. The decay process of the waste emitting α, β and γ radiation can take up to millions of years. This is problematic as within this time period the nuclear wastes must be isolated from biosphere; the migration of the radioactive materials to the biosphere causes adverse effects and is highly hazardous to all biological systems/organisms. Therefore the nuclear waste must be treated with an appropriate fashion, stored in properly engineered storage facility and must not impose undue burden for future generations (IAEA 2011). The classification of the nuclear waste depends on the waste management policy of each waste producing country, typically taking account of the radiation levels, decay activity and disposal issues. In this study, the classification of the waste, characterisation and the waste disposal management will be based on the current UK regulations and policies. The radioactive wastes in the UK are divided into three categories and the details are as follows:

2.3.1. High Level Waste

High Level Waste (HLW) is defined as waste "in which the temperature may rise significantly as a result of their radioactivity, so that this factor has to be taken into account in designing storage

or disposal facilities" (Her Majesty's Stationery Office 1995). Within the UK, HLW mainly existed in liquid form and is a by-product from the reprocessing of spent nuclear fuel; the process is carried out at Sellafield and will continue until 2018 (NDA and DECC 2013). Due to the heat generated and very high radiation levels, the HLW liquid requires continuous engineered cooling and substantial shielding. In order to increase the efficiency of the nuclear fuel cycle, the spent nuclear fuel reprocessing is aimed at recovering/extracting the (re-)usable uranium and plutonium. The extracted uranium and plutonium are later being recycled for the production of new fuel called mixed oxide (MOX) fuel. For immobilisation, the HLW liquid is calcined to become solid, mixed with alkali borosilicate glass frit and is converted into homogeneous glass by a vitrification process, poured into a stainless steel canister after which a lid is welded onto it (~150 litre capacity) and stored in an engineered air-cooled facility at Sellafield for at least 50 years to allow the reduction of radioactivity by natural decay processes; the current plan for final disposal of the HLW canisters is long term disposal in a geological disposal facility (Ojovan and Lee 2005, CoRWM 2006, Defra *et al* 2008, NDA 2009, DECC 2014).

2.3.2. Intermediate Level Waste

Intermediate Level Waste (ILW) is defined as waste "with radioactivity levels exceeding the upper boundaries for low level wastes, but which do not require heating to be taken into account in the design of storage or disposal facilities" (Her Majesty's Stationery Office 1995). The ILW may contain very long half live radionuclides, in particular, alpha emitting radionuclides and can require significant shielding during disposal process and storage (CoRWM 2006). Essentially, ILW comprises a wider range of materials than HLW and the major constituents of the waste include fuel cladding, irradiated graphite (see Section 2-4), contaminated reactor components and sludge from the treatment of radioactive liquid effluents. Typical treatment for ILW is cement encapsulation, packaged in 500 litre or higher volume containers manufactured from stainless steel, iron or concrete and temporarily stored in interim ILW storage at Berkeley, Bradwell, Hinkley Point A and Sizewell A; the final disposal plan of the ILW will be similar to the HLW namely in a geological disposal facility but not located in similar vault (Ojovan and Lee 2005, Lee *et al* 2013, Magnox and NDA 2013, DECC 2014).

2.3.3. Low Level Waste

Low Level Waste (LLW) is defined as "radioactive waste having a radioactive content not exceeding 4 GBq per tonne of alpha or 12 GBq per tonne of beta/gamma activity"; a sub-category of LLW is Very Low Level Waste (VLLW), which is split into two groups according to the specific disposal method as follows (Defra *et al* 2007):

- Low volume VLLW (dustbin loads) – Defined as "radioactive waste which can be safely disposed of in an unspecified destination with municipal, commercial or industry waste (dustbin disposal), each 0.1 m^3 of waste containing less than 400 kBq of total activity or single item containing less than 40 kBq of total activity". With respect to VLLW that contains ^{14}C and ^{3}H, the activity limits from both radionuclides is 4000 and 400 kBq in each 0.1 m^3 and for any single item respectively. No controls on disposal are needed when removing these wastes from premises to a disposal site.
- High volume VLLW (bulk disposals) – Defined as "radioactive waste with maximum concentration of 4 MBq per tonne of total activity which can be disposed of to specified landfill sites". The concentration limit for waste containing ^{3}H is 40 MBq per tonne. Controls on disposal specified by the environmental regulators are required when removing these wastes from premises to a disposal site.

In general, LLW and VLLW are materials that are lightly contaminated with radionuclides or materials that have been used in environment where radioactive materials are present. The volume of the wastes commonly arises from soil, metal components, building rubble, plastic, paper, protective clothing and laboratory equipment (Lee *et al* 2013). Since 1995, the LLW has been compacted in steel drums, stacked into larger containers, cement grouted and finally stored/disposed in an engineered concrete vault near Drigg, Cumbria (NDA 2010, 2011). The VLLW is either incinerated or undergoes controlled landfill disposal according to the aforementioned waste classification.

2.4. Irradiated Graphite

Irradiated graphite is a problematic waste resulting from the long term exposure of nuclear grade graphite or purified graphite to neutrons and mainly originates from gas-cooled nuclear power reactors. Currently, all the irradiated graphite waste producing countries have raised significant concerns about the management and disposal routes for the irradiated graphite waste. It is also worth mentioning that at present, there is no ideal solution for the final disposal of irradiated graphite (IAEA 2006, 2010). In addition, the complexity of irradiated graphite waste usually makes the handling (dismantling during decommissioning), transportation and waste packages challenging. Although the literature on the immobilisation of irradiated graphite waste is limited at the time being, in this section, it is intended to discuss the available literature about nuclear graphite, which includes the structure and properties of graphite, production of nuclear graphite, waste origin and volume, radiation effects on graphite and finally challenges for its waste immobilisation and disposal.

2.4.1. Structure and Properties of Graphite

Graphite is a crystalline allotrope of carbon that is made up from stacks of parallel aromatic or graphene layers. Each sp^2 hybridised carbon atom in the graphene layer plane is bonded with three other similar carbon atoms to form a series of continuous hexagons in a network (infinite two-dimensional molecule). There are 2 types of bonds present in the graphene layer; (i) sigma bond (covalent) between each carbon atom in the hexagon structure, the bond length is 0.141 nm and it has a high strength of 524 kJ/mole; (ii) π-bond (van der Waals) from the hybridised fourth valence electron located perpendicular to the graphene layer plane paired with another delocalised electron from the adjacent graphene layer plane, the spacing between the graphene layer plane is 0.335 nm (twice the van der Waals radius of carbon) and it has a low strength of 7 kJ/mole (Kelly 1981, Pierson 1993, Burchell 1999). The weak van der Waals bonds explains the soft characteristic of graphite which in general easily shears (cleaves) when force is applied. In nature, there are two known structures of graphite formed by different graphene staking sequences; -ABABAB- stacking for hexagonal graphite and -ABCABCABC- stacking for rhombohedral graphite (see Figure 2-2 and 2-3).

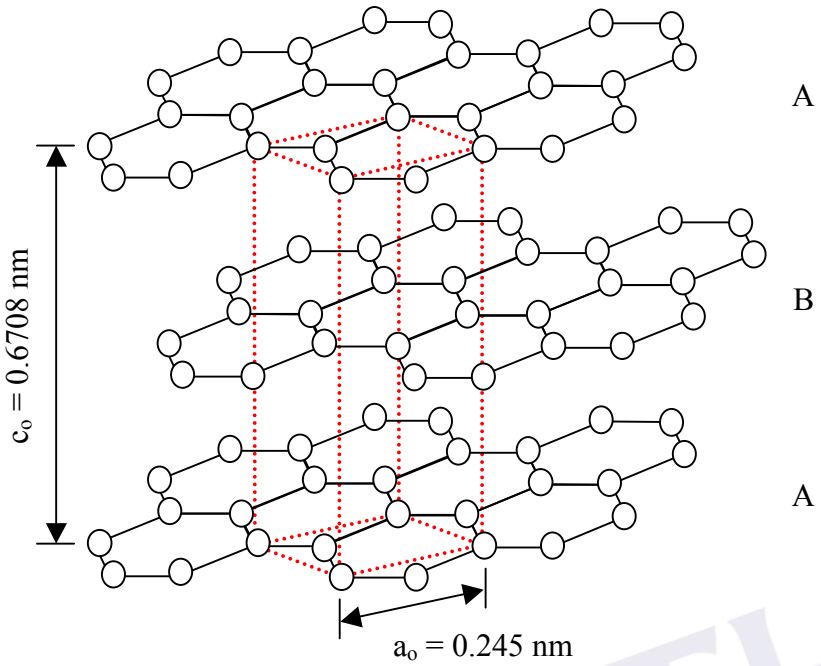

Figure 2-2: Hexagonal unit cell of graphite, space group: $D_{6h}^{4} - P6_3/mmc$ (Pierson 1993).

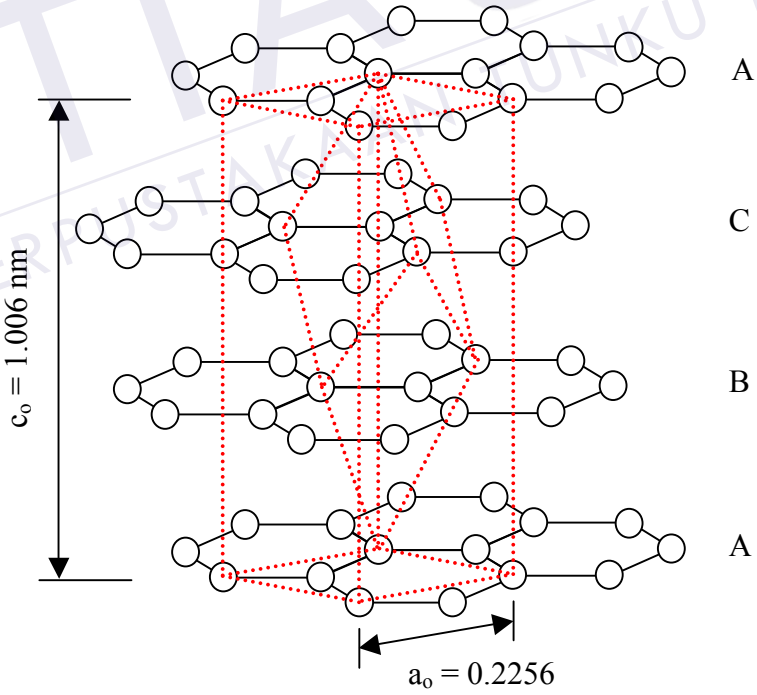

Figure 2-3: Rhombohedral unit cell of graphite, space group: $D_{3d}^{5} - R\bar{3}m$ (Reynolds 1968).

The hexagonal (alpha) structure of the graphite is thermodynamically stable and it is the commonest structure. In contrast, the rhombohedral (beta) graphite structure is thermodynamically unstable and the form is best known as an extended stacking fault of hexagonal graphite. The rhombohedral graphite is never found in the pure form and always exists in combination with hexagonal graphite. Normally natural and synthetic graphites contain a proportion of rhombohedrally structured material of which the amount found is typically less than 40 % (Pierson 1993, IAEA 2000). It is worthy of note that the content of rhombohedral graphite can be increased by grinding (shear deformation) and can also revert progressively to hexagonal graphite by heat treatment above 1300°C (Pierson 1993, IUPAC 1997).

As mentioned previously, graphite is used in the nuclear industry due to its capability to reduce the kinetic energy of fission neutrons by collisions (moderator in Section 2.2.1) and it has a low neutron cross-section *i.e.* the value is around 3.5-3.8 mb for pure nuclear graphite (Nightingale 1963). In addition, the properties of graphite such as being strong enough for structural components (produced by extrusion or vibration moulding or isostatic pressing), having good machinability, being stable and certified as one of the most inert materials make it highly attractive as well as suitable for many nuclear applications. The detailed properties of graphite can be seen in Tables 2-2 and 2-3; note that all the properties are based on the ideal graphite structure in powder form.

Table 2-2: Physical properties of graphite (Kelly 1981, Pierson 1993, Burchell 1999).

Property	Description
Colour	Black
Lattice parameters	See Figure 2-2
Atomic volume	5.315 cm^3/mol
Theoretical density (300 K, 1 atm)	2.26 g/cm^3
Melting point (estimated)	4450 K

References

Abdelouas A, Noirault S and Grambow B 2006 Immobilization of inert TRISO coated fuel in glass for geological disposal *J. Nucl. Mater.* **358** 1–9

Abid M, Et-tabirou M and Taibi M 2003 Structure and DC conductivity of lead sodium ultraphosphate glasses *Mater. Sci. Eng. B* **97** 20–4

Adamantiades A and Kessides I 2009 Nuclear power for sustainable development: current status and future prospects *Energy Policy* **37** 5149–66

Almeida F J M, Martinelli J R and Partiti C S M 2007 Characterization of iron phosphate glasses prepared by microwave heating *J. Non. Cryst. Solids* **353** 4783–91

Amjad Z and Zuhl R 2006 Kinetic and morphological investigation on the precipitation of calcium carbonate in the presence of inhibitors *Corrosion NACExpo 2006, 61st annual conference & exposition* p 6385

Andreev G E 1991 A review of the Brazilian test for rock tensile strength determination. Part I: calculation formula *Min. Sci. Technol.* **13** 445–56

Banhart F 1999 Irradiation effects in carbon nanostructures *Reports Prog. Phys.* **62** 1181–221

Barclay J and Carroll M 1996 Pre-eruptive volatile content and degassing history of an evolving peralkaline volcano *J. Volcanol. Geotherm. Res.* **74** 75–87

Bayliss S, Ewart F T, Howse R M, Dmith-Briggs J L, Thomason H P and Wilmott H A 1987 The solubility and sorption of lead-210 and carbon-14 in a near-field environment *Scientific Basis for Nuclear Waste Management XI, MRS Proceedings* vol 112 pp 33–42

Beckman Coulter Inc. 2011 Coulter LS series, product manual *TECDOC PN 4237214EA* 4–3

Béghein P, Berlioux G, Mesnildot B Du, Hiltmann F and Melin M 2012 NBG-17 - An improved graphite grade for HTRs and VHTRs *Nucl. Eng. Des.* **251** 146–9

Bingham P A, Hand R J and Forder S D 2006 Doping of iron phosphate glasses with Al_2O_3, SiO_2 or B_2O_3 for improved thermal stability *Mater. Res. Bull.* **41** 1622–30

Bingham P A, Hand R J, Forder S D and Lavaysierre A 2005 Vitrified metal finishing wastes: II. Thermal and structural characterisation *J. Hazard. Mater.* **122** 129–38

Bingham P A, Hand R J, Hannant O M, Forder S D and Kilcoyne S H 2009 Effects of modifier additions on the thermal properties, chemical durability, oxidation state and structure of iron phosphate glasses *J. Non. Cryst. Solids* **355** 1526–38

Bingham P A, Hyatt N C and Hand R J 2012 Vitrification of UK intermediate level radioactive wastes arising from site decommissioning: property modelling and selection of candidate host glass compositions *Glas. Technol. Eur. J. Glas. Sci. Technol. A* **53** 83–100

Bingham P a. and Jackson C M 2008 Roman blue-green bottle glass: chemical-optical analysis and high temperature viscosity modelling *J. Archaeol. Sci.* **35** 302–9

Birkel C S, Douglas J E, Lettiere B R, Seward G, Zhang Y, Pollock T M, Seshadri R and Stucky G D 2013 Influence of Ni nanoparticle addition and spark plasma sintering on the TiNiSn–Ni system: Structure, microstructure, and thermoelectric properties *Solid State Sci.* **26** 16–22

Bootjomchai C, Laopaiboon J, Nontachat S, Tipparach U and Laopaiboon R 2012 Structural investigation of borosilicate recycled-barium – bismuth glasses under the influence of gamma-irradiation through ultrasonic and FTIR studies *Nucl. Eng. Des.* **248** 28–34

Brown F J, Palmer J D and Wood P 1999 Derivation of a radionuclide inventory for irradiated graphite-chlorine-36 Inventory determination *Proc. IAEA Tech. Comm. Meet.* 143–52

Burchell T D 1999 *Carbon materiales for advanced technologies* (Pergamon: Elsevier Science Ltd., Oxford)

Burchell T D 2012 *Comprehensive nuclear materials: radiation effects in graphite* vol 4, ed R J M Konings (Elsevier Science Ltd., Oxford)

Burchell T D, Eatherly W P, Robbins J M and Strizak J P 1992 The effect of neutron irradiation on the structure and properties of carbon-carbon composite materials *J. Nucl. Mater.* **191-194** 295–9

Burchell T D and Snead L L 2007 The effect of neutron irradiation damage on the properties of grade NBG-10 graphite *J. Nucl. Mater.* **371** 18–27

Cassingham N J, Bingham P A, Hand R J and Forder S D 2008 Property modification of a high level nuclear waste borosilicate glass through the addition of Fe_2O_3 *Glas. Technol.* **49** 21–6

Chadwick J 1932 The existence of a neutron *Proc. R. Soc. A Math. Phys. Eng. Sci.* **136** 692–708

Chakraborty S and Arora A K 2012 Temperature evolution of Raman spectrum of iron phosphate glass *Vib. Spectrosc.* **61** 99–104

Chen Q, Tang C Y, Chan K C and Liu L 2013a Viscous flow during spark plasma sintering of Ti-based metallic glassy powders *J. Alloys Compd.* **557** 98–101

Chen Z, Lu P, Zhu H, Du B, Xie T, Wang W and Xu M 2013b AC impedance investigation and charge–discharge performance of NaOH surface-modified natural graphite *Electrochim. Acta* **102** 44–50

Choi E-Y, Han T H, Hong J, Kim J E, Lee S H, Kim H W and Kim S O 2010 Noncovalent functionalization of graphene with end-functional polymers *J. Mater. Chem.* **20** 1907–12 Online: See Supplementary Info

Cochran T B, Feiveson H A, Patterson W, Pshakin G, Ramana M V, Schneider M, Suzuki T and Hippel F V 2010 *Fast Breeder Reactor Programs: History and Status* vol 8 (International Panel on Fissile Materials)

Córdoba J M, Chicardi E, Poyato R, Gotor F J, Medri V, Guicciardi S and Melandri C 2013 Spark plasma sintering of $Ti_xTa_{1-x}C_{0.5}N_{0.5}$-based cermets: Effects of processing conditions on chemistry, microstructure and mechanical properties *Chem. Eng. J.* **230** 558–66

CoRWM 2006 Managing our radioactive waste safely: CoRWM's recommendations to government *CoRWM Doc 700*

Darwish H and Gomaa M M 2006 Effect of compositional changes on the structure and properties of alkali-alumino borosilicate glasses *J. Mater. Sci. Mater. Electron.* **17** 35–42

Day D E, Wu Z, Ray C S and Hrma P 1998 Chemically durable iron phosphate glass wasteforms *J. Non. Cryst. Solids* **241** 1–12

DECC 2013 Consultation review of the siting process for a geological disposal facility *URN 13D/250*

DECC 2014 Implementing geological disposal: a framework for the long-term management of higher activity radioactive waste *URN 14D/235*

Defra, BERR and the devolved administrations for Wales and Northen Ireland 2008 Managing radioactive waste safely: a framework for implementing geological disposal *Cm 7386*

Defra, DTI and Administrations D 2007 Policy for the long term management of solid low level radioactive waste in the United Kingdom *PB 12522*

Dickson D P E and Berry F J 1986 *Mossbauer spectroscopy* (Cambridge University Press)

Djohari H and Derby J J 2009 Transport mechanisms and densification during sintering: II. Grain boundaries *Chem. Eng. Sci.* **64** 3810–6

Djohari H, Martínez-Herrera J I and Derby J J 2009 Transport mechanisms and densification during sintering: I. Viscous flow versus vacancy diffusion *Chem. Eng. Sci.* **64** 3799–809

Donald I W 2010 *Waste immobilization in glass and ceramic based hosts: radioactive, toxic and hazardous wastes* (John Wiley & Sons Ltd, West Sussex)

Donald I W, Metcalfe B L and Taylor R N J 1997 Review: the immobilization of high level radioactive wastes using ceramics and glasses *J. Mater. Sci.* **32** 5851–87

Dubourg M 1998 Technologies fro gas cooled reactor decommissioning, fuel storage and waste disposal: the carbon 14 Cycle *IAEA TECDOC 1043* 233–7

Duderstadt J J and Hamilton L J 1976 *Nuclear reactor analysis* (John Wiley and Sons, Inc., New York)

Dunbar N W and Kyle P R 1992 Volatile contents of obsidian clasts in tephra from the Taupo Volcanic Zone, New Zealand: Implications to eruptive processes *J. Volcanol. Geotherm. Res.* **49** 127–45

Dunzik-Gougar M Lou and Smith T E 2014 Removal of carbon-14 from irradiated graphite *J. Nucl. Mater.* **451** 328–35

Dyar M D, Agresti D G, Schaefer M W, Grant C A and Sklute E C 2006 Mössbauer spectroscopy of earth and planetary materials *Annu. Rev. Earth Planet. Sci.* **34** 83–125

Einstein A 1905 Does the inertia of a body depend upon its energy-content? (Ist die Trägheit eines Körpers von seinem Energieinhalt abhängig?) *Ann. Phys.* 1–3

Elbouaanani L K, Malaman B and Gérardin R 1999 Structure refinement and magnetic properties of C–$Fe(PO_3)_3$ studied by neutron diffraction and Mössbauer techniques *J. Solid State Chem.* **148** 455–63

El-Egili K 2003 Infrared studies of $Na_2O - B_2O_3 - SiO_2$ and $Al_2O_3 - Na_2O - B_2O_3 - SiO_2$ glasses *Phys. B* **325** 340–8

Ericson J E, Makishima A, Mackenzie J D and Berger R 1975 Chemical and physical properties of obsidian: a naturally occuring glass *J. Non. Cryst. Solids* **17** 129–42

Ericsson T, Nord A G, Ahmed M M O, Gismelseed A and Khangi F 1990 $Fe_2P_2O_7$ and $Fe_2P_4O_{12}$ studied between 5–800 K *Hyperfine Interact.* **57** 2179–86

Fachinger J 2012 *Comprehensive nuclear materials: Graphite* vol 5, ed R J M Konings (Elsevier Science Ltd., Oxford)

Fachinger J, Grosse K H, Hrovat M and Seemann R 2012 Utilization of HTR reflector graphite as embedding matrix for radioactive waste *Nucl. Eng. Des.* **251** 235–8

Fachinger J, von Lensa W and Podruhzina T 2008 Decontamination of nuclear graphite *Nucl. Eng. Des.* **238** 3086–91

Forder S D, Bingham P A, McGann O J, Stennett M C and Hyatt N C 2012 Mössbauer studies of materials used to immobilise industrial wastes *Hyperfine Interact.* **217** 83–90

Fredrick D M, Gash A E, Landingham R L, Satcher J H and Munir Z a. 2013 Sol gel synthesis and spark plasma sintering of lanthana-doped alumina glass *J. Non. Cryst. Solids* **363** 64–9

Frenkel J 1945 Viscous flow of crystalline bodies under the action of surface tension *J. Phys. USSR* **9** 385–91

Frisch O R 1939 Physical evidence for the division of heavy nuclei under neutron bombardment *Nature* **143** 276–276

Furukawa T, Fox K E and White W B 1981 Raman spectroscopic investigation of the structure of silicate glasses. III. Raman intensities and structural units in sodium silicate glasses *J. Chem. Phys.* **75** 3226

Gaafar M S and Marzouk S Y 2007 Mechanical and structural studies on sodium borosilicate glasses doped with Er_2O_3 using ultrasonic velocity and FTIR spectroscopy *Phys. B* **388** 294–302

Galeener F L 1982 Planar rings in glasses *Solid State Commun.* **44** 1037–40

Garcia-lodeiro I, Fernández-jimenez A, Pena P and Palomo A 2014 Alkaline activation of synthetic aluminosilicate glass *Ceram. Int.* **40** 5547–58

Girke N A, Bushuev A V, Kozhin A F, Petrova E V, Aleeva T B and Zubarev V N 2012 ^{14}C in spent graphite from uranium-graphite reactors at the Siberian chemical combine *At. Energy* **112** 63–6

Goodhew P J, Humphreys F J and Beanland R 2001 *Electron microscopy and analysis* (Taylor & Francis, London)

Goodwin C, Barkatt A and Al-Sheikhly M 2014 On the mechanism of the interactions of neutrons and gamma radiation with nuclear graphite-implications to HTGRs *Radiat. Phys. Chem.* **97** 38–47

Greenwood N N and Earnshaw A 1997 *Chemistry of the elements* (Butterworth-Heinemann, Oxford)

Guillon O, Gonzalez-Julian J, Dargatz B, Kessel T, Schierning G, Räthel J and Herrmann M 2014 Field-assisted sintering technology/spark plasma sintering: mechanisms, materials, and technology developments *Adv. Eng. Mater.* **16** 830–49

Guiroy J J 1995 Graphite waste incineration in a fluidized bed *Spec. Meet. Graph. moderator lifecycle Behav.* 193–203

Guyon J, Hazotte A, Monchoux J P and Bouzy E 2013 Effect of powder state on spark plasma sintering of TiAl alloys *Intermetallics* **34** 94–100

Hafid M, Jermoumi T, Toreis N and Ghailassi T 2002 Structure of $(45-x)Na_2O–xBaO–5ZnO–50P_2O_5$ glasses studied by DSC and infrared spectroscopy *Mater. Lett.* **56** 486–90

Hall G, Marsden B J and Fok S L 2006 The microstructural modelling of nuclear grade graphite *J. Nucl. Mater.* **353** 12–8

Haynes W M 2014 *CRC handbook of chemistry and physics, 95th edition, 2014-2015* (CRC Press/Taylor and Francis, Boca Raton, FL)

Heath P G, Corkhill C L, Stennett M C, Hand R J, Meyer W C H M and Hyatt N C 2013 Encapsulation of TRISO particle fuel in durable soda-lime-silicate glasses *J. Nucl. Mater.* **436** 139–49

Heggie M I, Suarez-Martinez I, Davidson C and Haffenden G 2011 Buckle, ruck and tuck: a proposed new model for the response of graphite to neutron irradiation *J. Nucl. Mater.* **413** 150–5

Her Majesty's Stationery Office 1995 Review of radioactive waste management policy: final conclusions *Cm 2919*

Hietanfn R, Jaakkola T and Miettinen J K 1984 Sorption of cesium, strontiuli, iodine and carbon in concrete and sand *Scientific Basis for Nuclear Waste Management VIII, MRS Proceedings* vol 44 pp 891–8

Hisa M, Tsutsumi A and Akiyama T 2004 Reduction of iron oxides by nano-sized graphite particles observed in pre-oxidized iron carbide at temperatures around 873 K *Mater. Trans.* **45** 1907–10

Hrovat M, Grosse K-H and Seemann R 2013 Matrix material comprising graphite and an inorganic binder suited for final disposal of radioactive waste, a process for producing the same and its processing and use *US Patent, US 8502009 B2*

Huang C and Behrman E C 1991 Structure and properties of calcium aluminosilicate glasses *J. Non. Cryst. Solids* **128** 310–21

Huang S, Swarnakar A K, Vanmeensel K and Vleugels J 2013 Diamond dispersed Si3N4 composites obtained by pulsed electric current sintering *J. Eur. Ceram. Soc.* **33** 1237–47

Huang W, Day D E, Ray C S, Kim C-W and Mogus-Milankovic A 2004 Vitrification of high chrome oxide nuclear waste in iron phosphate glasses *J. Nucl. Mater.* **327** 46–57

Huang W-H, Tsai S-C, Yang C-W and Kai J-J 2014 The relationship between microstructure and oxidation effects of selected IG- and NBG-grade nuclear graphites *J. Nucl. Mater.* **454** 149–58

Hussainova I, Voltšihhin N, Cura E and Hannula S-P 2014 Densification and characterization of spark plasma sintered ZrC–ZrO_2 composites *Mater. Sci. Eng. A* **597** 75–81

IAEA 2013 Annual report 2013 *GC(58)/3*

IAEA 2006 Characterization, treatment and conditioning of radioactive graphite from decommissioning of nuclear reactors *TECDOC 1521*

IAEA 2011 Disposal of radioactive waste: specific safety requirements *No. SSR-5*

IAEA 2014a Energy, electricity and nuclear power estimates for the period up to 2050 *Ref. Data Ser. No. 1, 2014 Ed.*

IAEA 2000 Irradiation damage in graphite due to fast neutrons in fission and fusion systems *TECDOC 1154*

IAEA 2004 Management of waste containing tritium and carbon-14 *Tech. Reports Ser. No. 421*

IAEA 2007 Nuclear power plant design charateristics: structure of nuclear power plant design characteristics in the IAEA power reactor information system (PRIS) *TECDOC 1544*

IAEA 2014b Nuclear power reactor in the world *Ref. Data Ser. No. 2, 2014 Ed.*

IAEA 2010 Progress in radioactive graphite waste management *TECDOC 1647*

IEA 2014a Key world energy statistics *Inernational Energy Agency*

IEA 2014b World energy outlook *Inernational Energy Agency*

IUPAC 1997 *Compendium of chemical terminology (the "gold book")* ed A D McNaught, A Wilkinson and A Jenkins (Blackwell Scientific Publications, Oxford)

Jermoumi T, Hafid M, Niegisch N, Mennig M, Sabir A and Toreis N 2002 Properties of $(0.5-x)Zn–xFe_2O_3–0.5P_2O_5$ glasses *Mater. Res. Bull.* **37** 49–57

Joseph K, Premila M, Amarendra G, Govindan Kutty K V, Sundar C S and Vasudeva Rao P R 2012 Structure of cesium loaded iron phosphate glasses: an infrared and Raman spectroscopy study *J. Nucl. Mater.* **420** 49–53

Kalampounias A G 2011 IR and Raman spectroscopic studies of sol–gel derived alkaline-earth *Bull. Mater. Sci.* **34** 299–303

Kamitsos E 1996 Reply to "Comment on Infrared-reflectance spectra of heat-treated, sol-gel-derived silica" *Phys. Rev. B* **53** 14659–62

Kamitsos E I, Kapoutsis J A, Jain H and Hsieh C H 1994 Vibrational study of the role of trivalent ions in sodium trisilicate glass *J. Non. Cryst. Solids* **171** 31–45

Kang S-J L 2005 *Sintering: densification, grain growth and microstructure* (Elsevier Butterworth-Heinemann, Oxford)

Karabulut M, Metwalli E, Day D E and Brow R K 2003 Mössbauer and IR investigations of iron ultraphosphate glasses *J. Non. Cryst. Solids* **328** 199–206

Karlina O K, Klimov V L, Ojovan M I, Pavlova G Y, Dmitriev S A and Yurchenko A Y 2005 Immobilization of carbon-14 from reactor graphite waste by use of self-sustaining reaction in the C–Al–TiO_2 system *J. Nucl. Mater.* **345** 84–5

Kelly B T 1981 *Physics of graphite* (Applied Science Publishers, London)

Kelly B T and Burchell T D 1994 Structure-related property changes in polycrystalline graphite under neutron irradiation *Carbon N. Y.* **32** 499–505

Kharissova O V., Kharisov B I and Valdés J J R 2010 Review: the use of microwave irradiation in the processing of glasses and their composites *Ind. Eng. Chem. Res.* **49** 1457–66

Kim C-W and Day D E 2003 Immobilization of Hanford LAW in iron phosphate glasses *J. Non. Cryst. Solids* **331** 20–31

Kim T, Lee J and Lee K-H 2014 Microwave heating of carbon-based solid materials *Carbon Lett.* **15** 15–24

Kjeldsen J, Smedskjaer M M, Mauro J C, Youngman R E, Huang L and Yue Y 2013 Mixed alkaline earth effect in sodium aluminosilicate glasses *J. Non. Cryst. Solids* **369** 61–8

Lai Y, Liang X, Yang S, Liu P, Zeng Y and Hu C 2014 Raman and FTIR spectra of CeO_2 and Gd_2O_3 in iron phosphate glasses *J. Alloys Compd.* **617** 597–601

Lai Y, Liang X, Yin G, Yang S, Wang J, Zhu H and Yu H 2011a Infrared spectra of iron phosphate glasses with gadolinium oxide *J. Mol. Struct.* **1004** 188–92

Lai Y M, Liang X F, Yang S Y, Wang J X, Cao L H and Dai B 2011b Raman and FTIR spectra of iron phosphate glasses containing cerium *J. Mol. Struct.* **992** 84–8

Larkin P J 2011 *"IR and Raman spectroscopy - principles and spectral interpretation"* (Elsevier, USA)

Lee W E, Ojovan M I and Jantzen C M 2013 *Radioactive waste management and contaminated site clean-Up* (Woodhead Publishing Limited, Cambridge)

Lewis E E 2008 *Fundamentals of nuclear reactor physics* (Academic Press/Elsevier, Burlington, MA)

Lim Y S, Chi S H and Cho K Y 2008 Change of properties after oxidation of IG-11 graphite by air and CO_2 gas *J. Nucl. Mater.* **374** 123–8

Lipińska M E, Novais J P, Rebelo S L H, Bachiller-Baeza B, Rodríguez-Ramos I, Guerrero-Ruiz A and Freire C 2014 Microwave-assisted silylation of graphite oxide and iron(III) porphyrin intercalation *Polyhedron* **81** 475–84

Lowenstern J B, Bleick H, Vazquez J a., Castro J M and Larson P B 2012 Degassing of Cl, F, Li, and Be during extrusion and crystallization of the rhyolite dome at Volcán Chaitén, Chile during 2008 and 2009 *Bull. Volcanol.* **74** 2303–19

Ma L, Brow R K and Choudhury A 2014 Structural study of Na_2O–FeO–Fe_2O_3–P_2O_5 glasses by Raman and Mössbauer spectroscopy *J. Non. Cryst. Solids* **402** 64–73

MacDonald S A, Schardt C R, Masiello D J and Simmons J H 2000 Dispersion analysis of FTIR reflection measurements in silicate glasses *J. Non. Cryst. Solids* **275** 72–82

Mackenzie J K and Shuttleworth R 1949 A phenomenological theory of sintering *Proc. Phys. Soc. Sect. B* **62** 833–52

Magnox and NDA 2013 Intermediate level waste (ILW) storage and fuel element debris (FED) treatment optimisation study Online: http://www.nda.gov.uk/publication/intermediate-level-waste-ilw-storage-and-fuel-element-debris-fed-treatment-optimisation-study/

Mahdy E A and Ibrahim S 2012 Influence of Y_2O_3 on the structure and properties of calcium magnesium aluminosilicate glasses *J. Mol. Struct.* **1027** 81–6

Marasinghe G K, Karabulut M, Ray C S, Day D E, Shuh D K, Allen P O, Saboungi M L, Grimsditch M and Haeffner D 2000 Properties and structure of vitrified iron phosphate nuclear wasteforms *J. Non. Cryst. Solids* **263** 146–54

Márquez E, Piña G, Rodriguez M, Fachinger J, Grosse K, Luis J, Nieto L, Gracian M Q and Seemann R 2011 GRAFEC: a new spanish program to investigate waste management options for radioactive graphite *WM2012 Conference, February 26 – March 1, 2011, Phoenix, Arizona, USA*

Marzouk S Y, Seoudi R, Said D A and Mabrouk M S 2013 Linear and non-linear optics and FTIR characteristics of borosilicate glasses doped with gadolinium ions *Opt. Mater. (Amst).* **35** 2077–84

Mazo M A, Palencia C, Nistal A, Rubio F, Rubio J and Oteo J L 2012 Dense bulk silicon oxycarbide glasses obtained by spark plasma sintering *J. Eur. Ceram. Soc.* **32** 3369–78

Mazurin O V. 2007 Problems of compatibility of the values of glass transition temperatures published in the world literature *Glas. Phys. Chem.* **33** 22–36

Mazurin O V. and Gankin Y V. 2008 Glass transition temperature: problems of measurement procedures *Glass Technology: European Journal of Glass Science and Technology Part A* vol 49 pp 229–33

McGann O J, Bingham P A, Hand R J, Gandy A S, Kavčič M, Žitnik M, Bučar K, Edge R and Hyatt N C 2012 The effects of γ-radiation on model vitreous wasteforms intended for the disposal of intermediate and high level radioactive wastes in the United Kingdom *J. Nucl. Mater.* **429** 353–67

McGann O J and Ojovan M I 2011 The synthesis of graphite–glass composites intended for the immobilisation of waste irradiated graphite *J. Nucl. Mater.* **413** 47–52

Mcgill S L, Walkiewicz W E and Clark A E 1995 Microwave heating of chemicals and minerals *Rep. Investig. 9518*

McKeown D A, Buechele A C, Viragh C and Pegg I L 2010 Raman and X-ray absorption spectroscopic studies of hydrothermally altered alkali-borosilicate nuclear waste glass *J. Nucl. Mater.* **399** 13–25

McMillan P 1984 Structural studies of silicate glasses and melts-applications and limitations of Raman spectroscopy *Am. Mineral.* **69** 622–44

McMillan P and Piriou B 1982 The structures and vibrational spectra of crystals and glasses in the silica-alumina system *J. Non. Cryst. Solids* **53** 279–98

Mcmillan P, Piriou B and Navrotsky A 1982 A Raman spectroscopic study of glasses along the joins silica-calcium aluminate, silica-sodium aluminate, and silica-potassium aluminate *Geochim. Cosmochim. Acta*

Meitner L and Frisch O R 1939 Breaking up is easy - nuclear fission discovered *Nature* **143** 239–40

Menéndez J a., Arenillas A, Fidalgo B, Fernández Y, Zubizarreta L, Calvo E G and Bermúdez J M 2010 Microwave heating processes involving carbon materials *Fuel Process. Technol.* **91** 1–8

Menyah K and Wolde-Rufael Y 2010 CO_2 emissions, nuclear energy, renewable energy and economic growth in the US *Energy Policy* **38** 2911–5

Mercier M, Di Muro A, Giordano D, Métrich N, Lesne P, Pichavant M, Scaillet B, Clocchiatti R and Montagnac G 2009 Influence of glass polymerisation and oxidation on micro-Raman water analysis in alumino-silicate glasses *Geochim. Cosmochim. Acta* **73** 197–217

Meredith R J 1998 *Engineers' handbook of industrial microwave heating* (The Institution of Electrical Engineers, London)

Millet J M, Virely C, Forissier M, Bussière P and Vedrine J C 1989 Mössbauer spectroscopic study of iron phosphate catalysts used in selective oxidation *Hyperfine Interact.* **46** 619–28

Moguš-Milanković A, Šantić A, Reis S T, Furić K and Day D E 2004 Mixed ion–polaron transport in Na_2O–PbO–Fe_2O_3–P_2O_5 glasses *J. Non. Cryst. Solids* **342** 97–109

Mondal K, Lorethova H, Hippo E, Wiltowski T and Lalvani S B 2004 Reduction of iron oxide in carbon monoxide atmosphere-reaction controlled kinetics *Fuel Process. Technol.* **86** 33–47

Morgan L E, Renne P R, Taylor R E and WoldeGabriel G 2009 Archaeological age constraints from extrusion ages of obsidian: examples from the middle Awash, Ethiopia *Quat. Geochronol.* **4** 193–203

Mughabghab S F, Divadeenam M, Holden N E, Kinsey R R and McLane V 1981 *Neutron cross section series* ed S F Mughabghab, R R Kinsey and C L Dunford (Academic Press Inc. (London) Ltd.)

Mysen B O 1990 Interaction between water and melt in the system $CaAl_2O_4$-SiO_2-H_2O *Chem. Geol.* **88** 223–43

Mysen B O, Virgo D and Seifert F A 1982 The stucture of silicate melts: implications for chemical and physical properties of natural magma *Rev. Geophys. Sp. Phys.* **20** 353–83

Nakahara M and Sanada Y 1995 FT-IR ATR spectroscopy of the edge surface of pyrolytic graphite and its surface/PVC interface *J. Mater. Sci.* **30** 4363–8

NDA 2011 UK Management of solid low level radioactive waste from the nuclear industry: low level waste strategic review *NLWS/LLWR/16*

NDA 2009 UK radioactive higher activity waste storage review UK radioactive higher activity waste storage review Online: http://www.nda.gov.uk/publication/uk-radioactive-higher-activity-waste-storage-review-march-2009/

NDA 2010 UK strategy for the management of solid low level radioactive waste from the nuclear industry Online: http://www.nda.gov.uk/publication/uk-strategy-for-the-management-of-solid-low-level-radioactive-waste-from-the-nuclear-industry-august-2010/

NDA and DECC 2013 Radioactive wastes in the UK: a summary of the 2013 inventory Online: https://www.nda.gov.uk/wp-content/uploads/sites/2/2014/02/14D039-NDASTSTY140006-UKRWI-2013-High-Level-Summary.pdf

Neuville D, Cormier L and Massiot D 2006 Al coordination and speciation in calcium aluminosilicate glasses: Effects of composition determined by 27Al MQ-MAS NMR and Raman spectroscopy *Chem. Geol.* **229** 173–85

Neuville D R, Cormier L and Massiot D 2004 Al environment in tectosilicate and peraluminous glasses: A 27Al MQ-MAS NMR, Raman, and XANES investigation *Geochim. Cosmochim. Acta* **68** 5071–9

Niehues J, Lehmann P and Xie W 2012 Low coherent Linnik interferometer optimized for use in nano-measuring machines *Meas. Sci. Technol.* **23** 125002

Nightingale R E 1963 *Nuclear graphite* vol 47 (Academic Press Inc. (London) Ltd)

OECD, NEA and IEA 2015 Technology roadmap: nuclear energy Online: https://www.iea.org/publications/freepublications/publication/TechnologyRoadmapNuclearEnergy.pdf

OECD Nuclear Energy Agency 2014 Technology roadmap update for generation IV nuclear energy systems Online: https://www.gen-4.org/gif/upload/docs/application/pdf/2014-03/gif-tru2014.pdf

Ojovan M I 2011 *Handbook of advanced radioactive waste conditioning technologies* (Woodhead Publishing Limited, Cambridge)

Ojovan M I and Lee W E 2005 *An introduction to nuclear waste immobilisation* (Elsevier Ltd., Oxford)

Olanipekun O, Oyefusi A, Neelgund G M and Oki A 2014 Adsorption of lead over graphite oxide. *Spectrochim. Acta. A. Mol. Biomol. Spectrosc.* **118** 857–60

Pichon C, Guy C and Comte J 2008 ^{36}Cl and ^{14}C behaviour in UNGG graphite during leaching experiments *Commun. Ref. number* 1–5

Pierson H O 1993 *Handbook of carbon, graphite, diamond and fullerenes: properties, processing and applications* (Noyes Publications, New Jersey)

Piotrowski K, Wiltowski T, Mondal K, Stonawski L, Szymański T and Dasgupta D 2005 Simultaneous influence of gas mixture composition and process temperature on $Fe_2O_3 \rightarrow FeO$ reduction kinetics - Neural network modeling *Brazilian J. Chem. Eng.* **22** 419–32

Plodinec M J 2000 Borosilicate glasses for nuclear waste imobilisation *Glas. Technol.* **41** 186–92

Podruzhina T 2004 Graphite as radioactive waste; corrosion behaviour under final repository conditions and thermal treatment *Inst. für Sicherheitsforsch. und Reakt. Jül-4166*

Prado M O and Zanotto E D 2002 Glass sintering with concurrent crystallization *Comptes Rendus Chim.* **5** 773–86

Premila M, Abhaya S, Rajaraman R, Ravindran T R, Amarendra G and Sundar C S 2012 Probing the local structural changes across the amorphous to crystalline transition in iron phosphate glass: Positron annihilation and micro Raman studies *J. Non. Cryst. Solids* **358** 1014–8

Qian B, Liang X, Yang S, He S and Gao L 2012 Effects of lanthanum addition on the structure and properties of iron phosphate glasses *J. Mol. Struct.* **1027** 31–5

Rajkumar K and Aravindan S 2009 Microwave sintering of copper–graphite composites *J. Mater. Process. Technol.* **209** 5601–5

Rao K J, Vaidhyanathan B, Ganguli M and Ramakrishnan P A 1999 Synthesis of inorganic solids using microwaves *Chem. Mater.* **11** 882–95

Rappeneau J, Taupin J L and Grehier J 1966 Energy released at high temperature by irradiated graphite *Carbon N. Y.* **4** 115–24

Reynolds W N 1968 *Physical properties of graphite* (Elsevier Publishing Co. Ltd., New York)

Ristić M M and Milosević S D 2006 Frenkel's theory of Sintering *Sci. Sinter.* **38** 7–11

Rizzo S, Grasso S, Salvo M, Casalegno V, Reece M J and Ferraris M 2014 Joining of C/SiC composites by spark plasma sintering technique *J. Eur. Ceram. Soc.* **34** 903–13

Rublevskiy V P 2012 Commercial nuclear reactors and 14C *At. Energy* **113** 117–20

Rupesh Kumar A, Rao T G V M, Neeraja K, Rami Reddy M and Veeraiah N 2013 Gamma ray induced changes on vibrational spectroscopic properties of strontium alumino-borosilicate glasses *Vib. Spectrosc.* **69** 49–56

Saddeek Y B, Gaafar M S and Bashier S A 2010 Structural influence of PbO by means of FTIR and acoustics on calcium alumino-borosilicate glass system *J. Non. Cryst. Solids* **356** 1089–95

Saheb N, Iqbal Z, Khalil A, Hakeem A S, Al Aqeeli N, Laoui T, Al-Qutub A and Kirchner R 2012 Spark plasma sintering of metals and metal matrix nanocomposites: a review *J. Nanomater.* **2012** 1–13

Sahin F C, Kanbur H E and Apak B 2012 Preparation of AlON ceramics via reactive spark plasma sintering *J. Eur. Ceram. Soc.* **32** 925–9

Schofield J M 2011 *Vitrification of a chloride containing actinide waste surrogate* (The University of Sheffield)

Schofield J M, Bingham P A and Hand R J 2009 The immobilisation of a chloride containing actinide waste surrogate in calcium aluminosilicate glasses *Environ. Issues Waste Manag. Technol. Mater. Nucl. Ind. XII. Ceram. Trans.* **207** 69–80

Schroeder J, Wu W, Apkarian J L, Lee M, Hwa L-G and Moynihan C T 2004 Raman scattering and Boson peaks in glasses: temperature and pressure effects *J. Non. Cryst. Solids* **349** 88–97

Schweitzer D G and Singer R M 1965 Oxidation rates of alternately irradiated and annealed graphite *J. Nucl. Mater.* **16** 220–6

Seifert F A, Mysen B O and Virgo D 1982 Three-dimensional network structure of quenched melts (glass) in the systems SiO_2-$NaAlO_2$, SiO_2-$CaAl_2O_4$ and SiO_2-$MgAl_2O_4$. *Am. Mineral.* **67** 696–717

Sengupta P 2012 A review on immobilization of phosphate containing high level nuclear wastes within glass matrix - present status and future challenges *J. Hazard. Mater.* **235-236** 17–28

Serne R J, Lokken R O and Criscenti L J 1992 Characterization of grouted low-level waste to support performance assessment *Waste Manag.* **12** 271–87

Shelby J E 2005 *Introduction to glass science and technology* (The Royal Society of Chemistry, Cambridge)

Smith B 2011 *Fundamentals of fourier transform infrared spectroscopy* (CRC Press/Taylor and Francis, Boca Raton, FL)

Socrates G 2004 *Infrared and Raman characteristic group frequencies* (John Wiley and Sons., West Sussex)

Song S, Wen Z, Liu Y, Zhang Q, Wu X, Zhang J and Han J 2009 Influence of dopants on the crystallization of borosilicate glass *Ceram. Int.* **35** 3037–42

Sontakke A D, Biswas K and Annapurna K 2009 Concentration-dependent luminescence of Tb3+ ions in high calcium aluminosilicate glasses *J. Lumin.* **129** 1347–55

Środa M and Paluszkiewicz C 2008 The structural role of alkaline earth ions in oxyfluoride aluminosilicate glasses-Infrared spectroscopy study *Vib. Spectrosc.* **48** 246–50

Stacey W M 2007 *Nuclear reactor physics* (WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim)

Stennett M C and Hyatt N C 2009 Microwave processing of glasses for waste immobilization *Scientific Basis for Nuclear Waste Management XXXII, MRS Proceedings* vol 1124 pp 147–52

Stennett M C, Pinnock I J and Hyatt N C 2011 Rapid synthesis of $Pb_5(VO_4)_3I$, for the immobilisation of iodine radioisotopes, by microwave dielectric heating *J. Nucl. Mater.* **414** 352–9

Suárez M, Fernández A and Menéndez J 2013 Challenges and opportunities for spark plasma sintering: a key technology for a new generation of materials *Sintering Applications* ed B Ertug

Tamayo A, Mazo M A, Rubio F and Rubio J 2014 Structure properties relationship in silicon oxycarbide glasses obtained by spark plasma sintering *Ceram. Int.* **40** 11351–8

Telling R H and Heggie M I 2007 Radiation defects in graphite *Philos. Mag.* **87** 4797–846

Thostenson E T and Chou T W 1999 Microwave processing: fundamentals and applications *Compos. Part A Appl. Sci. Manuf.* **30** 1055–71

Tokita M 1999 Mechanism of spark plasma sintering *Proceeding of NEDO International Symposium on Functionally Graded Materials* vol 21 p 22

Vidhyanathan B, Ganguli M and Rao K J 1994 A novel method of preparation of inorganic glasses by microwave irradiation *J. Solid State Chem.* **113** 448–50

Vogel N, Nomade S, Negash A and Renne P R 2006 Forensic $^{40}Ar/^{39}Ar$ dating: a provenance study of middle stone age obsidian artifacts from Ethiopia *J. Archaeol. Sci.* **33** 1749–65

Vulpius D, Baginski K, Fischer C and Thomauske B 2013 Location and chemical bond of radionuclides in neutron-irradiated nuclear graphite *J. Nucl. Mater.* **438** 163–77

Wang J-S, Jeng J-S and Ni C-T 2009 The study on the phosphate glass melted by microwave irradiation *J. Non. Cryst. Solids* **355** 780–4

Wang X and Dou W 2012 Preparation of graphite oxide (GO) and the thermal stability of silicone rubber/GO nanocomposites *Thermochim. Acta* **529** 25–8

Westrich H R, Stockman H W and Eichelberger J C 1988 Degassing of rhyolitic magma during ascent and emplacement *J. Geophys. Res.* **93** 6503

White I F, Smith G M, Sauders L J, Kaye C J, Martin T J, Clarke G H and Wakerley M W 1984 Assessment of Management Modes for Graphite from Reactor Decommissioning *Comm. Eur. Communities EUR 9232* 1–119

White W B and Minser D G 1984 Raman spectra and stuctural of natural glasses *J. Non. Cryst. Solids* **67** 45–59

Wickham A J, Neighbour G B and Dubourg M 1999 The uncertain future for nuclear graphite disposal: crisis or opportunity? *Proceedings of the Technical Committee Meeting on Nuclear Graphite Waste Management* (Manchester, UK) pp 1–16

Wilson P D 1996 *The nuclear fuel cycle: from ore to wastes* (Oxford University Press)

Windes W, Burchell T and Bratton R 2007 Graphite technology development plan *Idaho Natl. Lab. PLN-2497, Rev 0*

Winterstein-Beckmann A, Möncke D, Palles D, Kamitsos E I and Wondraczek L 2014 A Raman-spectroscopic study of indentation-induced structural changes in technical alkali-borosilicate glasses with varying silicate network connectivity *J. Non. Cryst. Solids* **405** 196–206

WNA 2015 Nuclear Power Reactors *World Nucl. Assoc.* Online: http://www.world-nuclear.org/info/Nuclear-Fuel-Cycle/Power-Reactors/Nuclear-Power-Reactors/

Xie G 2013 Spark plasma sintering: a useful technique to develop large-sized bulk metallic glasses *J. Powder Metall. Min.* **2** 2–4

Yang G, Möbus G and Hand R J 2006 Cerium and boron chemistry in doped borosilicate glasses examined by EELS *Micron* **37** 433–41

Yim M-S and Caron F 2006 Life cycle and management of carbon-14 from nuclear power generation *Prog. Nucl. Energy* **48** 2–36

Yu Y-H, Lin Y-Y, Lin C-H, Chan C-C and Huang Y-C 2014 High-performance polystyrene/graphene-based nanocomposites with excellent anti-corrosion properties *Polym. Chem.* **5** 535

Zhang C, Chen M, Xu X, Zhang L, Zhang L, Xia F, Li X, Liu Y, Hu W and Gao J 2014 Graphene oxide reduced and modified by environmentally friendly glycylglycine and its excellent catalytic performance *Nanotechnology* **25** 135707

Zhang J, Tu R and Goto T 2012 Fabrication of transparent SiO_2 glass by pressureless sintering and spark plasma sintering *Ceram. Int.* **38** 2673–8